Spatial variability of nitrate concentration in lakes in Snowdonia, North Wales, UK

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Abstract

At a regional scale, high nitrate (NO_3^-) concentrations in upland surface waters generally occur in tandem with high nitrogen (N) deposition levels. However, significant differences in the patterns of surface water NO_3^- concentration have been observed within areas of similar N deposition yet relatively few studies have been undertaken which examine within-region variation of NO_3^- concentrations. A study of 76 lakes in Snowdonia, north Wales, an area of high deposition and sensitive catchments, was undertaken to assess variation in surface water NO_3^- concentration across a 20 × 20 km grid square and to identify catchments vulnerable to NO_3^- leaching. Nitrate concentrations vary considerably, particularly during winter when values range from 0.7 to 70 μeq l^{-1}. Although retention by vegetation and soil microbes in summer reduces the amount of NO_3^- reaching the lakes, 37% of sites are characterised by NO_3^- concentrations greater than 4 μeq l^{-1}. The elevated concentrations occurring in summer suggests that N breakthrough has occurred. By examining the ratio of NO_3^- to total strong acid anions, it is shown that NO_3^- contributes significantly to freshwater acidity, particularly during the winter. Redundancy analysis shows that NO_3^- leaching is greatest, both in winter and summer, in catchments with high proportions of bare rock where soil and vegetation cover is limited. Nitrogen cycling in these catchments, generally at higher altitudes, may no longer be governed by seasonal biological controls. They are likely to be saturated with respect to nitrogen (i.e. incapable of further N retention) as a result of the elevated deposition levels in the area. The contribution of NO_3^- to acidity is also greatest at these sites. In winter, significant positive relationships are also evident between NO_3^- concentration and soil pH and coniferous woodland. The study demonstrates the importance of catchment factors in modifying the relationship between N deposition and N leaching in upland catchments.

Introduction

Until recently, most assessments of the effects of acidification on surface waters have focused on the role of sulphur (S) deposition (e.g. Harriman and Wells, 1985; Henriksen *et al.*, 1990; Forsius *et al.*, 1992; CLAG, 1995; Battarbee *et al.*, 1996). However, across Europe, S emissions have declined substantially and are expected to continue doing so in future (RGAR, 1997). Over the same period, emissions of oxidised nitrogen (NO_x) have remained relatively stable with slight increases in some areas (RGAR, 1997; Vincent *et al.*, 1997). Trends in reduced nitrogen are more difficult to quantify as sources are much more diffuse (RGAR, 1997). The contribution of nitrogen (N) to total acid deposition is thus becoming more important (RGAR, 1997). Coincident with this has been evidence of increasing levels of nitrate (NO_3^-) in upland waters (e.g. Stoddard, 1994; UKAWMN, 1997; Henriksen *et al.*, 1997) and predictions of further increases in future (Curtis *et al.*, 1998).

The pattern of surface water NO_3^- concentrations across the UK indicates that surface waters in upland areas of England and Wales and SW Scotland are vulnerable to acidification due to NO_3^- leaching (Allott *et al.*, 1995; Harriman *et al.*, 1995). Many freshwater sites in these areas currently exhibit NO_3^- leaching in runoff (Jenkins *et al.*, 1997) and, in high deposition areas of Great Britain (e.g. North Wales, Lake District, Pennines), the contribution of NO_3^- to the sum of strong acid anions can reach 40% (Jenkins *et al.*, 1996; Curtis *et al.*, 1998).

Although it has been demonstrated that, at a regional scale, patterns of NO_3^- concentration in surface waters are broadly consistent with N deposition levels (INDITE, 1994; Allott *et al.*, 1995; Jenkins *et al.*, 1996), nitrate leaching can vary significantly between proximal catchments (Stevens *et al.*, 1993) and between areas which have similar N deposition levels (Reynolds *et al.*, 1992; Emmett *et al.*, 1993; Curtis *et al.*, 1998). There is, however, relatively little information relating to within-region variation in N leaching.

This paper describes the results of a case study of lake catchments within a 20 × 20 km area of North Wales, UK. Initially, variation in the NO_3^- concentration of lakes in the

study area is examined to identify those catchments where leaching of NO_3^- (i.e. N breakthrough) is occurring. The contribution of nitrogen to the acidity of the study lakes is also considered using the N-acidification ratio (NAR) proposed by Henriksen *et al.*, (1997).

Secondly, catchment types that are currently most vulnerable to acidification from atmospheric N deposition are identified. The processes and mechanisms which determine the nature of the impact of N deposition on surface waters are more complex than those governing response to S alone. Although concentrations of NO_3^- in upland surface waters tend to be greater in areas of high N deposition (Allott *et al.*, 1995; Jenkins *et al.*, 1996), there is little direct evidence linking the two (Stoddard, 1994). The extent and timing of NO_3^- leaching and the precise factors controlling N breakthrough on a catchment scale are poorly understood (INDITE, 1994; Reynolds *et al.*, 1994) due to the complex process interactions governing catchment response to N deposition. It is known that the N flux within a catchment is regulated by a number of key processes including fixation, mineralisation, immobilisation, nitrification, denitrification, and assimilation by plants and soil microbes (see Reynolds *et al.*, 1992; Van Miegroet and Johnson, 1993; Reynolds and Edwards, 1995; Stoddard, 1994). These processes are mediated by the soil, biota and hydrological pathways within the contributing catchment, which in turn are largely determined by the physical characteristics of the catchment. The nature and rate of N transformation in the soil is influenced by soil type, temperature, moisture, nutrient status and chemical composition (e.g. Reynolds *et al.*, 1992; Cresser *et al.*, 1993; Stoddard, 1994; Dise and Wright, 1995). Vegetation type and maturity (particularly where forestry is the major land use) govern seasonal uptake rates (Emmett *et al.*, 1993). Additionally, the hydrological controls on N cycling in the catchment which determine flow pathways and residence time can also have a significant impact on streamwater NO_3^- concentration (Reynolds and Edwards, 1995; Kaste *et al.*, 1997).

To evaluate the relationships between the spatial variation in nitrate and ammonium observed in the study area and catchment characteristics, numerous variables derived from national databases are related empirically to the chemistry data using multivariate statistical techniques. In the absence of explicit, catchment-specific data relating to the processes and attributes outlined above, national soil and land cover datasets were employed to act as surrogates for soil and vegetation characteristics. These data include variables reflecting the physical and chemical status of the soil, the nature of the vegetation in the catchment, the physical characteristics of the catchment together with values relating to specific processes (i.e. denitrification and immobilisation). The study area was selected so as to minimise fertiliser inputs as a source of nitrogen. Most sites within the square are upland catchments with very limited managed grassland and no arable land.

Methods

STUDY AREA

The study area comprises a 20 × 20 km grid square in North Wales within the Snowdonia National Park, with Snowdon situated to the north-west (Figure 1). This is an area of high rainfall. Annual rainfall in the Upper Glaslyn catchment has been measured at approximately 2800 mm (Edwards *et al.*, 1990). Acid deposition in Wales is closely related to patterns of rainfall and, in the study area generally, exceeds 0.6 kg H^+ ha^{-1} yr^{-1} (Donald *et al.*, 1990). Mean annual wet deposition (interpolated from a monitoring network) at 20 km resolution for non-seasalt sulphate, nitrate and ammonium are >16 kg S ha^{-1} yr^{-1}, >8 kg N ha^{-1} yr^{-1} and >8 kg N ha^{-1} yr^{-1}, respectively. These are among the highest deposition values in the UK (RGAR, 1997). Previous work has shown that, at higher resolution, acid deposition and rainfall vary spatially across the area, the variation being driven by the complex local topography (Reynolds *et al.*, 1990).

The study area is geologically complex. Generally, Ordovician sedimentary formations (predominantly shales and slates) are dominant. Snowdon itself mainly comprises layered pyroclastic rocks, basaltic tuffs and rhyolitic lavas (the Snowdon Volcanic Series) which are underlain by grits and graptolitic slates of Llandeilo and Llanvirn age (Williams and Ramsay, 1959). These layered volcanics and the sedimentary formations are interspersed with acid doleritic dykes, rhyolitic tuff extrusions and granophyre intrusions (Williams and Ramsay, 1959). Ordovician volcanic and other igneous rocks characterise the higher ground in the study area and are much more resistant to denudation than the softer sedimentary formations (Smith and George, 1948). Towards the south, Cambrian shales, slates and mudstones dominate, intruded by doleritic dykes and a large granitic mass near Blaenau Ffestiniog. Much of the study area is underlain by geology which offers little or no buffering capacity (e.g. the acid igneous rocks) although some of the intermediate igneous rocks and the Ordovician shales are less sensitive (Edmunds and Kinniburgh, 1986).

Soils vary throughout the study area. Raw oligo-amorphous peat soils (Crowdy 1 and 2 associations) are dominant in the south-east and central areas. To the north-east and south-west, the area is characterised primarily by brown podzolic soil cover (Malvern and Manod series, respectively), interspersed with areas of humic rankers (Bangor series) which tend to overlie the rhyolitic geology of the more elevated topography. Other soils occurring include ferric stagnopodzols to the north and in the south-east (Hafren series) and humic brown podzols to the north east (Moor Gate series). Soils in the wetter, high altitude areas tend to be leached intensely and, as a consequence, more acidic (Thompson and Loveland, 1985). Detailed descriptions of these soil associations are provided by Rudeforth *et al.*, (1984) while the structure and

chemistry of soils in Snowdonia are examined by Ball *et al.*, (1969).

Land cover varies from the bare ground found at the higher altitudes to areas of improved grassland in the valley bottoms. Generally the area is dominated by upland and lowland moor. There are large areas of plantation forestry (primarily Sitka Spruce, *Picea sitchensis* (Bong. (Carr))) to the north west and, in a discontinuous belt, across the southern extent of the study area. A band of high relief, from the mountainous Glyder Fach/Fawr and Snowdon systems (bisected by the Pass of Llanberis) to the elevated semi-natural moorland centred on Cnicht and Moel-ry-hydd (separated from Snowdon by the Glaslyn valley) runs longitudinally along the eastern half of the study area. The east of the study area is characterised by semi-natural moorland and blanket bog with the deeper, raw acid peats of the Migneint Plateau to the south east. In the central area around Blaenau Ffestiniog, slate mining is evident in a number of catchments.

SITES AND SAMPLING METHODOLOGY

Nitrate concentrations in surface waters are typically characterised by strong seasonality (Stoddard, 1994). Each lake (76 sites) in the study area was sampled for water chemistry in February 1996 (to target minimum N retention by the soil and biota and therefore potential maximum leaching conditions) and July 1996 (to target maximum N retention and thus minimum leaching conditions) using a single spot sample, from the lake outflow, on both occasions. Table 1 provides a list of the lakes included in this study together with the altitude of the sample site and the maximum catchment altitude. The location of sites sampled in the study area is shown in Fig. 1. Water samples were refrigerated following collection and delivered to the Freshwater Fisheries Laboratory, Pitlochry within three days of sampling. After filtering, the samples were analysed for a suite of chemical determinands (including base cations, major anions, nutrients, pH and alkalinity) according to the methods described in Harriman *et al.*, (1990).

SECONDARY DATA

Catchment boundaries were digitised from 1:25,000 Ordnance Survey (OS) maps using the Geographical Information System, ARC/INFO. For each catchment, land cover data were obtained from the 25 m resolution

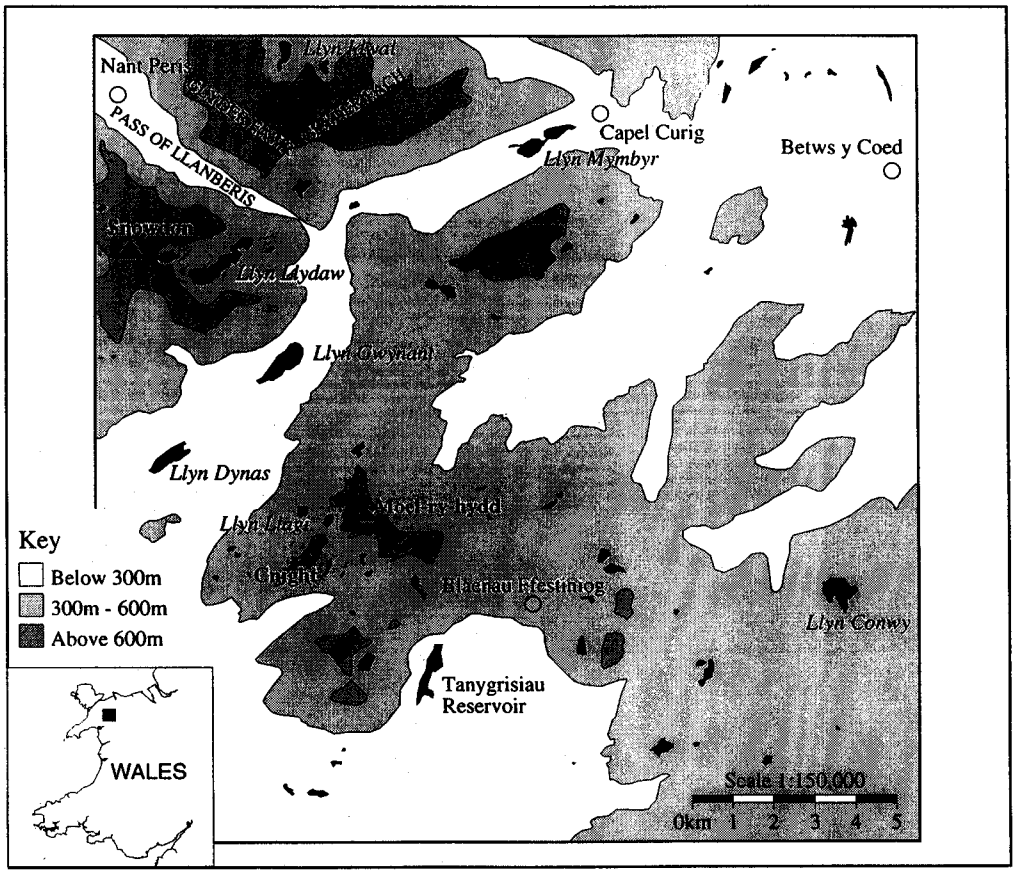

Fig. 1: *Map of study area, a 20 km grid square in North Wales indicating the location of sampled lakes and patterns of relief.*

Table 1. List of Snowdonia study sites with grid references, site altitude and maximum catchment altitude

Site name	Site Code	Easting	Northing	Site altitude (m)	Maximum catchment altitude (m)	Site name	Site Code	Easting	Northing	Site altitude (m)	Maximum catchment altitude (m)
Llyn y Cwn	AR26A	263700	358500	711	999	Llyn Dinas	SNSH6427	261600	349600	60	1085
Llyn Cwmffynnon	CFYN	265000	356400	390	999	Quarry 1	SNSH6501	260100	352100	490	747
Llyn Conwy	CON	278000	346300	450	527	Level	SNSH6502	260400	352600	580	704
Llyn Glas	CZSH65	261800	355700	640	1001	Llyn Glas	SNSH6503	261100	355700	530	1050
Llyn Foel	CZSH75	271400	354800	560	872	Llyn Clyd	SNSH6504	263500	359700	610	947
Llynau Diwaunydd	DIWA	268500	353700	370	872	Llyn y Dywarchen	SNSH7401	276300	342000	500	513
Glaslyn	DW24B	261700	354600	464	1085	Llyn Morwynion	SNSH7403	273700	342500	400	552
Llyn Edno	EDNO	266300	349700	500	607	Llyn Serw	SNSH7404	277900	342800	450	460
Llynnau Gamallt 1	GAM	274800	344300	460	580	Llynnau Gamallt 2	SNSH7405	274600	344400	460	500
Llyn Idwal	IDWA	264500	359600	380	999	Un-named 2	SNSH7406	274100	345700	420	500
Llyn Llagi	LAG	264800	348300	380	672	Llyn Dubach	SNSH7407	274500	342400	400	410
Llyn Mair	MAIR	265300	341300	80	258	Llyn Bowydd	SNSH7409	272500	346700	480	658
Llyn Ffridd-y-bwlch	SNSH6401	269500	348100	320	698	Llyn Newydd	SNSH7410	272300	347200	480	586
Llyn Drynogydd	SNSH6402	269300	348800	440	524	Llyn Barlwyd 1	SNSH7411	271000	348400	450	620
Tanygrisiau	SNSH6403	268000	344100	180	770	Llyn Barlwyd 2	SNSH7412	271300	348600	450	620
Llyn Stwlan	SNSH6404	266400	344500	510	770	Llyn Manod	SNSH7413	271700	344700	400	661
Llyn y-Garnedd-uchaf	SNSH6405	265800	342400	250	710	Llyn Cefn	SNSH7414	271500	341900	300	310
Llyn y Garnedd	SNSH6406	265700	342000	230	710	Llyn u-bach	SNSH7415	272000	346000	440	648
Llyn Hafod-y-llyn	SNSH6407	264500	341400	130	234	Llynnau Mymbyr	SNSH7501	271000	357500	184	872
Llyn Hafod-y-llyn	SNSH6408	260000	344700	30	56	Reservoir 3	SNSH7502	272300	355900	380	750
Llyn Iwerddon	SNSH6409	268500	347800	480	698	Reservoir 4	SNSH7503	273200	355400	350	550
Llyn Cwmorthin	SNSH6410	267700	346400	330	698	Reservoir 5	SNSH7504	274800	354300	230	342
Llyn Conglog	SNSH6411	267400	347500	610	698	Llyn Bychan	SNSH7505	275200	359400	270	405
Llyn Coch	SNSH6412	266800	347700	630	676	Llyn Bodgynydd	SNSH7506	276000	359400	250	320
Llyn Croesor	SNSH6413	266100	345700	520	648	Llyn Goddionduon	SNSH7507	275400	358500	250	310
Llyn Clogwyn-brith	SNSH6414	266500	346700	530	550	Reservoir 1	SNSH7508	276500	359700	260	320
Llyn Cwm-corsiog	SNSH6415	266400	347000	530	676	Reservoir 2	SNSH7510	277400	359100	260	332
Llynnau 'r Cwn 1	SNSH6416	266400	348700	640	670	Llyn Parc	SNSH7513	279400	358600	214	298
Llynnau 'r Cwn 2	SNSH6417	266200	348800	610	670	Llyn Teryn	TEYR	264200	354700	380	550
Llynnau 'r Cwn 3	SNSH6418	266200	348600	630	660	Llyn Llydaw	VSH6502	263000	354400	440	1085
Llynnau Diffwys 1	SNSH6419	265900	346800	520	553	Quarry 2	VSH6504	260400	352200	500	704
Llynnau Diffwys 2	SNSH6420	265800	346600	520	553	Ceunant-y-Carnedd	VSH6505	269700	353100	360	872
Llyn Cwm-y-foel	SNSH6421	265500	346700	450	672	Llyn 'r Arrdu	VSH6506	260100	355700	580	1065
Llyn y Biswail	SNSH6422	264900	347400	550	689	Llyn Bochlywd	VSH6508	265500	359300	510	994
Un-named 1	SNSH6423	263500	346600	360	458	Llyn Lockwood	VSH6511	266300	355800	270	360
Llynnau Carrig-y-myllt 1	SNSH6424	263300	347200	420	463	Llyn Gwynant	VSH6513	264500	351800	170	1085
Llynnau Carrig-y-myllt 2	SNSH6425	263200	347400	420	463	Llyn Elsi	WSH7501	278400	355400	240	262
Llyn yr Arddi	SNSH6426	262800	346600	350	463	Llyn yr Adar	YRAD	265500	348000	580	672

LANDSAT TM database held at ITE Monks Wood (Fuller *et al.*, 1994). The digitised catchment boundaries were superimposed onto this using ARC/INFO and the percentage of each land class in each catchment was derived. The original 25 class dataset was combined into series of aggregated variables, shown in Table 2.

Each catchment was characterised according to a number of physical and chemical soil attributes (Table 2). These were derived by overlaying digital catchment boundaries onto the 1:250,000 soil map of Wales to obtain the proportion of each soil association therein. The soil series in each association were subsequently estimated using *a priori* knowledge (I. Bradley, pers. comm.). A range of values for the physical and chemical attributes (SSLRC derivation in Table 2) for each soil series was obtained, on an individual horizon basis, from soil profile data held at SSLRC (Bradley, pers. comm). Single values for each profile were derived by weighting according to horizon thickness. A series value was produced by averaging the profile values across each series. Averaged values for each catchment were calculated, the averages being weighted by the percentage occurrence within the catchment. Series with missing data were excluded from the weighting procedure.

Immobilisation and denitrification values have been estimated for UK soil types ranging between 1–3 and 1–4 kg ha^{-1} yr^{-1}, respectively (Hall *et al.*, 1997). Fixation is incorporated into the immobilisation term (Posch *et al.*, 1997). Using the weighting approach outlined above, single spatially weighted immobilisation and denitrification values were allocated to each of the study catchments.

Measured rainfall and runoff data were not available for individual catchments. Area weighted values for these variables were derived from the 1 km square resolution national databases held at the Institute of Hydrology. OS maps were used to provide information on altitude, catchment and lake size.

ANALYTICAL TECHNIQUES

To examine the relationships between catchment attributes and NO_3^-, concentration redundancy analysis (RDA) (Van den Wollenburg, 1977) was undertaken. This technique allows the variation in NO_3^- concentration accounted for by

Table 2. Summary of catchment variables used in the statistical analyses

Code	Variable	Derivation	Explanation
BD	Bulk density	SSLRC	* Catchment weighted soil bulk density
CEC	Cation exchange capacity	SSLRC	* Catchment weighted soil cation exchange capacity
Ca_soil	Ca in soil	SSLRC	* Catchment weighted soil Ca
Mg_soil	Mg in soil	SSLRC	* Catchment weighted soil Mg
K_soil	K in soil	SSLRC	* Catchment weighted soil K
Na_soil	Na in soil	SSLRC	* Catchment weighted soil Na
pH_soil	Soil pH	SSLRC	* Catchment weighted soil pH
Soil_OC	Organic carbon in soil	SSLRC	* Catchment weighted soil organic carbon
Top_OC	OC in top soil horizons	SSLRC	* Catchment weighted soil OC in upper horizons
Sub_OC	OC in sub-surface horizons	SSLRC	* Catchment weighted soil OC in lower horizons
Porosity	Soil porosity	SSLRC	* Catchment weighted soil porosity
Depth	Depth of soil	SSLRC	* Catchment weighted soil depth
N_imm	Nitrogen immobilisation	Hall *et al.*, 1997	* Catchment weighted Nitrogen immobilisation
N_den	Nitrogen denitrification	Hall *et al.*, 1997	* Catchment weighted Nitrogen denitrification
Rain	Rainfall (mm/yr)	ITE Monks Wood	Catchment weighted rainfall
Runoff	Runoff (mm/yr)	ITE Monks Wood	Catchment weighted runoff
L_area	Lake area (m^2)	GIS—OS Map	Lake area
C_area	Catchment area (km^2)	GIS—OS Map	Catchment area
L:C	Lake to catchment ratio	GIS	
Alt_s	Site altitude (m)	OS Map	Altitude of lake
Alt_m	Maximum altitude (m)	OS Map	Highest point in catchment
Unclass	% unclassified	ITE Monks Wood	Land cover type 'Not classified'
G_moor	% Grass/moorland	ITE Monks Wood	Lowland semi—natural grass / moor
G_m_upl	% Upland grass/moorland	ITE Monks Wood	Upland semi—natural grass moor
Agric_g	% Agricultural grassland	ITE Monks Wood	Arable and agricultural grassland
Wood_dec	% Deciduous woodland	ITE Monks Wood	Deciduous woodland
Wood_con	% Coniferous woodland	ITE Monks Wood	Coniferous woodland
Bare	% Bare ground	ITE Monks Wood	Bare ground

* Weighted averaging equation—$[x]_c = \Sigma A_s.[x]_s / \Sigma A_s$ where $[x]_c$ is a value for some physical or physical soil attribute for the catchment, A_s is the area of soil map series s and $[x]_s$ is the value for this attribute for soil map series s. The denominator Σ is taken over soil map series s_1 ... s_n.

the catchment attributes to be quantified. RDA models response data as a function of the explanatory data (ter Braak, 1994). RDA was implemented using CANOCO Version 3.10 (ter Braak, 1987) and the results were plotted using CALIBRATE (Juggins and ter Braak, 1993).

Results

VARIATION IN NITRATE AND AMMONIUM CONCENTRATION

Lake-water NO_3^- concentration varied considerably throughout the study area in both seasons (Table 3). The distribution of NO_3^- values in surface waters across the study area is shown for winter and summer by Fig. 2, a scatterplot with histograms, which highlights the different distributions between the two seasons. In winter, mean NO_3^- across all lakes was 24 μeq l^{-1} with a standard deviation (S.D.) of 12.3 and minimum and maximum values of 0.7 and 70 μeq l^{-1}, respectively. In summer, with more N taken up by the biomass, NO_3^- concentrations were lower. The mean value was 5.5 μeq l^{-1} (S.D. 7.7) with minimum and maximum values of zero and 34 μeq l^{-1}, respectively. Comparison with studies from stream sites in central and north Wales reveal similar patterns of winter mean nitrate values, although summer means in the study sites are comparatively low (cf. Reynolds *et al.*, 1994; Stevens *et al.*, 1997). Concentrations of surface water NO_3^- in upland grass/moorland catchments often exhibit summer minima and winter maxima (Edwards *et al.*, 1985; Reynolds *et al.*, 1992). This pattern is also observed in upland afforested catchments (Roberts *et al.*, 1984; Reynolds *et al.*, 1989) although summer maxima have also been noted in forest streams (Stevens *et al.*, 1993). Nitrogen cycling in pristine environments is dominated by plant and microbial uptake with measurable concentrations of oxidised and reduced N only occurring following snowmelt or storm conditions (Stoddard, 1994). At nearly all study sites, nitrate levels are higher during the winter when biological activity in the catchments is reduced. However, there are a number of lakes on or around the 1:1 line where summer and winter NO_3^- concentrations are similar (Fig. 2). Most of these sites (e.g. AR26A, DW24B, VSH6506) are among the highest altitude lakes in the study area. With one exception, all study lakes have winter NO_3^- values greater than the 4 μeq l^{-1} proposed by Kämäri *et al.*, (1992) as a background level for lakes in northern Norway receiving little acid deposition (although it should be noted that surface waters in low deposition areas of northern Scotland have NO_3^- concentrations < 1 μeq l^{-1}). Even during the growing season, 37% of lakes exceed this value, indicating incomplete assimilation of N into the terrestrial biomass. Where NH_4^+ has been detected (at about half the lakes) concentrations are generally low although maximum values

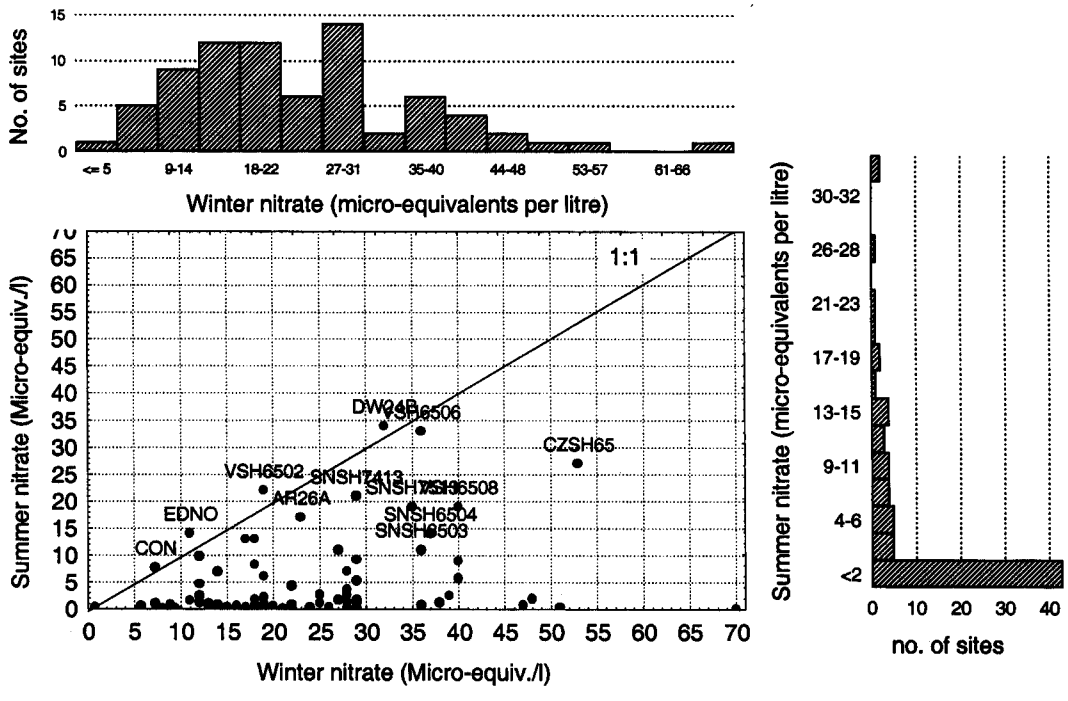

Fig 2: *Scatterplot with histograms illustrating the relationship between NO_3^- concentration in study lakes for winter and summer samples. The NO_3^- distribution across the summer and winter samples is illustrated by the histograms*

Table 3. Summary statistics: NO_3^-, NH_4^+, pH, Alkalinity and SO_4^{2-}, in the 76 study lakes

		No.	Min.	Max.	Median	Mean	Range	Variance	Std. Dev.
NO_3^-	Winter	76	0.7	70.0	22.0	24.3	69.3	152.4	12.3
	Summer	76	0.0	34.0	1.6	5.5	34.0	60.21	7.8
NH_4^+	Winter	76	0.0	7.0	2.0	1.7	7.0	2.7	1.7
	Summer	76	0.0	13.0	0.0	2.3	13.0	7.4	27
pH	Winter	76	4.2	6.9	5.4	5.4	2.7	0.41	0.64
	Summer	76	4.2	7.3	5.9	5.8	3.1	0.49	0.7
Alk	Winter	76	–66	438	4.5	16.7	504	3596	60
	Summer	76	–58	440	26.5	46.5	498	5410	73.5
SO_4^{2-}	Winter	76	36	187	60.6	71.3	150	897	29.9
	Summer	76	38	212	58.7	68.9	174	827	28.7

All units (except pH) in microequivalents per litre. Non marine sulphate is shown

of 13 μeq l^{-1} and 7 μeq l^{-1} were observed in summer and winter, respectively (Table 3). The acid status of lakes across the area also varies considerably (Table 3). For the winter sample, pH ranged from 4.2 to 6.9. For the same sample, alkalinity varied between –66 and 438 μeq l^{-1}. This gradient of acidity reflects the heterogeneity of lake/catchment systems across the study area. Alkalinity and pH in winter and summer exhibit similar ranges and do not display the seasonality of NO_3^- concentration. Sulphate varies between 36 and 187 μeq l^{-1} in winter and 38 and 187 μeq l^{-1} in summer. Median values of *c.* 60 μeq l^{-1} are generally higher than those found in upland environments in northern Europe as a result of the high sulphur deposition levels in this area (cf. Henriksen *et al.*, 1998). Table 4 shows how mean NO_3^- concentration varies across a series of pH classes. For the summer sample, when NO_3^- concentrations are low across the entire study area, the relationship between pH and NO_3^- is not statistically significant (r = 0.18; p = 0.116). During winter a weak positive relationship is observed (r = 0.24; p = 0.035) indicated by the changing NO_3^- mean across the pH classes. The relationships between NAR and pH (winter and summer samples) are not statistically significant. Mean NAR values are similar across pH classes. These relationships show that NO_3^- is not only leaching into lakes in the more sensitive catchments but may also be influencing acidity in less sensitive lakes. Given the acidifying potential of NO_3^-, an inverse relationship might be expected between the pH and NO_3^- at poorly buffered acid sensitive sites, driven primarily by variation in deposition levels. However, across the study area, where a range of catchment sensitivity is apparent, high NO_3^- values in catchments with well buffered soils and geology are likely to be associated with higher pH values as NO_3^- ions leaching into the lakes will be accompanied by base cations rather than hydrogen or aluminium ions.

CONTRIBUTION OF NO_3^- TO MINERAL ACIDITY

The contribution of NO_3^- to total non-marine acid anions can be assessed by examining NO_3^- as a proportion of mineral acidity (NO_3^-/NO_3^- + non-marine SO_4^{2-}). This has been termed the N-acidification ratio (Henriksen *et al.*, 1997). Figure 3 shows cumulative frequency curves for the N-acidification ratio (NAR) for the winter and summer samples. In winter, NAR varies between just above zero to 0.5 and at almost 50% of the lakes NO_3^- contributes over 25% of total mineral acidity. Comparison with the cumulative frequency curve of NAR for the July samples highlights the effect of seasonality on the relative contribution of NO_3^- to strong anion concentration. The summer samples have a much more skewed NAR distribution relative to winter NAR, (which approximates a normal distribution). Almost 75% of lakes have summer NAR values of less than 0.1 suggesting that the biomass utilisation of N

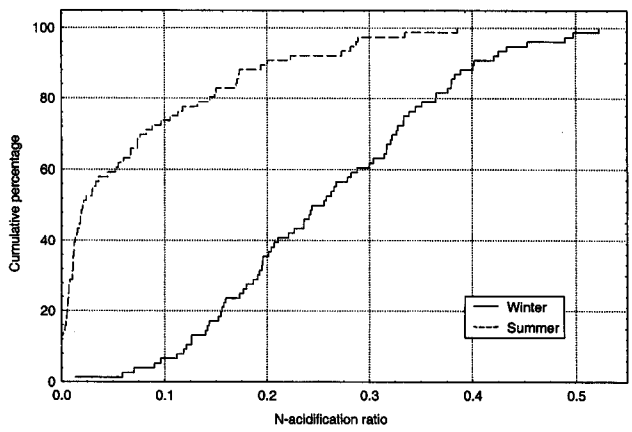

Figure 3: *Cumulative frequency curves for N-acidification ratio (winter and summer)*

Table 4. Variation in NO_3^- concentration (μeq l^{-1}) and NAR across pH classes

	pH Class	<5.0	5.0–5.5	>5.5–6.0	>6.0–6.5	>6.5
NO_3^-	Winter	19.9	27.5	21.9	28.7	31.5
	Summer	2.8	1.9	6.4	8.2	4.8
NAR	Winter	0.23	0.29	0.25	0.28	0.17
	Summer	0.04	0.03	0.08	0.11	0.05

All values expressed as means

species is buffering the surface waters against N derived acidity in summer, reducing its importance relative to the contribution of non-marine SO_4^{2-}.

RELATIONSHIP BETWEEN NO_3^-, NH_4^+, NAR AND CATCHMENT ATTRIBUTES

Redundancy analysis (RDA) was undertaken using NO_3^-, NH_4^+ and NAR from both the winter and summer samples as response variables and the variables representing catchment attributes (described above) as explanatory variables. The purpose was to produce a correlation biplot (Fig. 4) which allows the structure of the relationships between the chemical determinands and catchment variables to be explored synoptically. Chemical and catchment variables are plotted, together with sites, relative to ordination axes. These axes represent the primary gradients of variation within the structure of the data, both in terms of the chemistry and the catchment variables, the former constrained to be linear combinations of the latter. The vectors point in the direction of maximum variation, the length being proportional to this variation. Where the angle between vectors is acute, the variables are inferred to be positively correlated, the correlation increasing proportionally with the length of the vector. Obtuse angles signify negative correlations. The angles described between variable vectors and the axes can be interpreted similarly so that a variable with a long vector describing an acute angle with Axis 1 is highly correlated with it. The position of the sites in the biplot initially depends on chemical composition. Sites are arranged so that the distance between them reflects their dissimilarity. The position of a site relative to the arrowhead of a chemical or catchment vector indicates approximately where that site lies along the range of that variable.

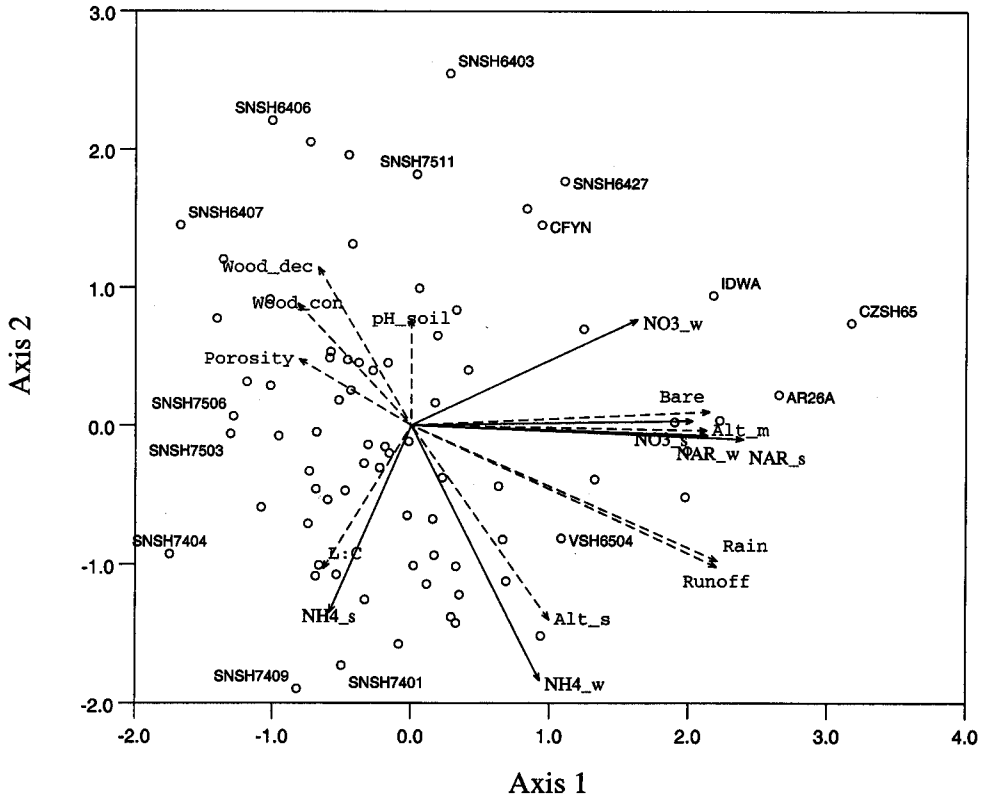

Fig. 4 *Redundancy analysis correlation biplot of chemistry (solid vectors) and catchment (broken vectors) variables (Plotted using CALIBRATE – Juggins and ter Braak, 1993). Sites are represented by open circles. The chemistry and catchment variable vectors have been multiplied ×4 for clarity. Variables with very short vectors have been omitted. Response variables have been centred and standardised See Table 2 for variable codings.*

Figure 4 shows that the main chemical gradient is associated with variation in NO_3^- and NAR, both in winter and summer. Sites vary positively along this axis so that lakes with high values for these variables (e.g. AR26A, CZSH65) are positioned to the right of the biplot. Axis 2 is associated with summer and winter NH_4^+ with the latter exhibiting the greater variance. The key catchment variables driving the variation along Axis 1 are rainfall, percentage bare ground (Bare) and maximum catchment altitude (Alt_m). Inter-set correlations between Axis 1 and all other variables have moduli of <0.5 indicating that they do not contribute substantially to variation in NO_3^- and NAR (ter Braak, 1990). Axis 2 is associated mostly with variation in site altitude (Alt_s), lake to catchment ratio (L:C), soil pH (pH_soil) and deciduous woodland (Wood_dec). However, none of these variables has inter-set correlations with a modulus >0.5 suggesting that factors outside those represented by the variables used in these analyses are responsible for variation in NH_4^+. It may be that local, catchment specific mechanisms (e.g. clearfelling or upland pasture improvement) may be more important here. Given this and the low levels of ammonium in the study area, subsequent analysis undertaken on NO_3^- and NAR was not repeated for NH_4^+.

The majority of land cover and soil variables do not appear influential in the analysis. A previous empirical study (Dise and Wright, 1995) also used a large number of catchment variables (including many of the soil chemistry variables used here) which were not significantly correlated with N leaching and concluded that either the importance of these were overshadowed by N deposition or that there were insufficient data to assess their importance.

To assess the level of explanation offered by the catchment attributes, a series of RDAs was undertaken using NO_3^- and NAR as individual response variables. This approach results in a single constrained axis (ter Braak, 1987) and is akin to multiple regression with the eigenvalue for this axis indicating how much of the variation in the response variable can be explained by the catchment attributes. To eliminate collinearity and reduce the likelihood of spurious explanation often associated with large numbers of predictors (Økland and Eilertson, 1994), forward selection was implemented in CANOCO. This allows a minimum set of statistically significant variables to be identified that explain the chemistry data almost as well as the full set (ter Braak, 1990). Variables are selected iteratively and the significance of each is tested using Monte Carlo permutations (ter Braak, 1990). Table 5 summarises the results of these analyses. The catchment data account for much more of the variation in NAR than NO_3^- in both the winter and summer samples. The greatest difference in NO_3^- concentration appears to be between vegetated and non-vegetated catchments as evidenced by the importance of percentage bare ground which accounts for 25% and 28% of the NO_3^- variation in the winter and summer samples, respectively. Catchments dominated by bare ground (with limited vegetation and little soil cover) are associated with high NO_3^- concentrations. Whereas percentage bare ground is the only explanatory variable identified following forward selection of the summer data, soil pH and percentage coniferous woodland also explain a small but statistically significant amount of variation in NO_3^- in the winter sample. In summer, bare ground is also the dominant explanatory variable in terms of NAR values, accounting for over half the variance. Rainfall is also

Table 5. Catchment attributes identified as significantly explaining variation in NO_3^-, and NAR. Monte Carlo Permutation tests were used to determine significance, initially at the 5% level. Thereafter, Bonferroni adjustment was used to prevent too many variables being judged significant (Manly, 1992)

Response Variable	Total Variance Explained	Significant explanatory variables (with cumulative extra fit). – see table 2 for definitions – signs indicate positive (+) or negative (–) relationships
NO_3^- (winter)	24.6%	Bare (13%)+, pH_soil (20%)+, Wood_con (25%)+
NO_3^- (summer)	27.7%	Bare (28%)+
NAR (winter)	51.6%	Runoff (48%)+,L:C(52%)+
NAR (summer)	46.2%	Bare (39%)+,Rainfall (46%)+

NB: Inferred correlations in Fig 4 area based on multivariate relationships between explanatory and response variables across more than one gradient. In RDA with a single response variable there is only gradient and this may explain why the vectors plotted in Fig 4 suggests a negative relationship between coniferous woodland and NO_3^- concentration whereas the forward selection procedure indicates the converse.

statistically significant during summer. In the winter sample, variation in NAR is predominantly explained by runoff (48%) with an additional 4% accounted for by lake to catchment ratio.

Discussion

Nitrate concentrations varied substantially across the study area. In summer these ranged from zero to 34 μeq l^{-1} although most sites exhibited concentrations considerably lower than this upper limit. Similar levels occur in stream sites throughout upland Wales (Reynolds *et al.*, 1994). For the winter sample, the range extends to 70 μeq l^{-1} which is very high for upland areas where, typically, concentrations are <8 μeq l^{-1} (Reynolds and Edwards, 1995) Most of the study lakes are characterised by lower NO_3^- concentrations during the growing season. Seasonal variation of N deposition may be a factor with higher fluxes reported during winter months (Donald *et al.*, 1990; Reynolds *et al.*, 1992; INDITE, 1994). However, it is clear that NO_3^- is also leaching in summer from a large number of sites and at some the seasonal signal is absent (see Fig. 2). Elevated NO_3^- concentrations during the growing season suggest a dampening of the seasonal pattern in N cycling and may indicate that catchments are saturated (i.e. incapable of further N retention (Aber, 1992). Although N is still being cycled in these systems, the leaching evident during the summer suggests that the pool of available N exceeds the biological and microbial uptake requirements.

At many sites, NO_3^- contributes significantly to acidity as measured by the N-acidification ratio (NAR). This ratio also exhibits a strong seasonality. Nitrate makes a significant contribution to the acidity of runoff primarily during the winter months. However, at a number of sites NO_3^- also contributes significantly to acidity during the growing season (NAR > 0.2 at 10% of sites). Similar ranges for NAR have been noted at upland sites throughout the UK (Jenkins *et al.*, 1996), in heavily impacted areas in Europe (Henriksen and Brakke, 1989; Henriksen *et al.*, 1997) and in North America (Stoddard, 1994).

The key variables driving variation in lake-water NO_3^- concentration and NAR were found to be percentage bare ground in the catchment together with runoff and rainfall. Catchments with a high proportion of bare ground tend to exhibit elevated lake NO_3^- and NAR levels. These catchments, generally at higher altitudes, have limited soil or vegetation cover and therefore lack the N retention capabilities of forest and moorland catchments where the demand for N is high during the growing season. Additionally, at higher altitudes where thin soils, steep slopes and high precipitation levels combine to produce high runoff, the role of soil and vegetation in N retention may be superseded by hydrological controls (Kaste *et al.*, 1997). Under these conditions the interaction between the N in soil solution and the soil and biota is reduced. Rainfall accounts for an additional 7% of the NO_3^- variation in the summer sample. Higher lake-water NO_3^- levels are found in catchments with higher rainfall. In summer, 48% of NAR variation is explained by runoff alone. The influence of the variables representing runoff and rainfall may be due to the coincidence of high runoff, thin soils and steep slopes at elevated altitudes, coupled with orographically enhanced precipitation levels. The amount of bare ground in the catchment is less important in winter because the reduced biological processes outside the growing season means there is less contrast between catchments with little soil and vegetation and those where soils are deeper and vegetation more abundant. It may be that N leaching to surface waters is driven by catchment hydrology during winter whereas biological controls are more important during the growing season. However, without more detailed, catchment specific, soil and deposition data, it is not possible to determine whether leaching at these sites is due to hydrological factors or as a result of N saturation (or some combination of both).

In the winter sample, a combination of percentage coniferous woodland and soil pH is responsible for almost half the explained NO_3^- variation (Table 5). Both vary positively with NO_3^- concentration. The role of forestry in N cycling and deposition scavenging is well documented (e.g. Fowler *et al.*, 1989; Reynolds *et al.*, 1989). Increased NO_3^- leaching from forested catchments has been observed in mid and north Wales where N inputs exceed tree and microbial requirements (Stevens *et al.*, 1994). Stand age has been found to be of particular significance with NO_3^- concentrations increasing with plantation age (Reynolds *et al.*, 1994; Stevens *et al.*, 1992). Although data relating specifically to stand age were not available for this study, observations in the field confirmed that most forestry in the catchments sampled is relatively mature, suggesting that the effects of N deposition onto the forest canopy are of more significance than uptake. Additionally, there are other processes impacted by forestry which may influence N leaching including mineralisation and nitrification in forest floor soils beneath mature trees (Emmett *et al.*, 1993; Reynolds *et al.*, 1994). Seasonality in NO_3^- concentrations has been observed in older forests where the large amounts of mineral N in the soil accumulated in the summer are leached out following autumn rains (Reynolds *et al.*, 1994) which is in keeping with the positive relationships identified between coniferous woodland and NO_3^- concentration in the winter sample.

The significance of soil pH in the winter sample is not clear. The positive relationship between soil pH and lake water NO_3^- concentration in winter indicates that catchments where the former is relatively high are associated with elevated NO_3^- concentrations. Traditionally, production of NO_3^- through nitrification was thought to be favoured by high soil pH (e.g. Aber *et al.*, 1989) although it is now believed that nitrification does occur in very acid soils (Gundersen and Rassmussen, 1990) assuming the supply of NH_4^+ is adequate (Stoddard, 1994). In areas of high

N deposition, catchments with deep soils and gentle slopes are characterised by longer soil water residence times which can lead to increased pools of soil N and enhanced nitrification (Dise and Wright, 1995). Conversely, increased runoff from thin acid soils overlying steep slopes can bypass the biological controls on N cycling and raise NO_3^- levels in surface waters (Kaste *et al.*, 1997). Indeed, nitrate leaching to surface waters may be associated with high or low soil pH (Dise and Wright, 1995). In the study area, the catchments with the lowest pH values occur on the acid raw peats in the south east whereas higher soil pH is found in catchments with high proportions of coniferous forestry planted on deeper mineral soils. It may be that the significance of soil pH in this analysis is an artefact, reflecting the mechanisms which give rise to elevated NO_3^- concentrations in forested catchments.

Lake to catchment ratio (L:C) is also statistically significant in the winter sample explaining an extra 4% extra of the variation in NAR with catchments with high NAR values characterised by low lake to catchment ratios. This relationship is primarily driven by high altitude lakes with low L:C values but high proportions of bare ground. In-lake retention of N is a function of runoff and lake to catchment area ratio (Kelly *et al.*, 1987). Thus the increased contribution of NO_3^- to acidity in these lakes may be due to a combination of thin soils and sparse vegetation in the catchment and the greater N retention in systems with low lake to catchment ratios (e.g. Henriksen, 1994) where flushing rates are much greater than in catchments where these are higher.

Although the high altitude, bare rock catchments appear to be most vulnerable to the effects of N deposition, given the lack of high resolution deposition data it is not possible to determine whether the relationships between NO_3^- and % bare ground is catchment driven or whether they reflect different deposition inputs due to altitudinal enhancements (Fowler *et al.*, 1988) as catchments with thin soils and sparse vegetation tend to occur at higher altitudes. However, bare ground is the single most important variable explaining variation in both NO_3^- and NAR suggesting that these relationships are not exclusively deposition driven because S deposition is also enhanced at altitude (RGAR, 1997). Thus if deposition alone were responsible for elevated NO_3^- concentrations at higher altitudes, it is likely that the strong relationship between NAR and % bare ground would be less apparent.

Although the empirical relationships described here are not based on explicit parameterisation of the key processes and mechanisms involved in N cycling, the use of surrogates for these, based on soil physical and chemical attributes and land cover, is intended to represent the catchment characteristics which determine response to atmospheric N deposition. However, the variables used in these analyses do not represent several important mechanisms and attributes which have been identified as key modifiers of N cycling in catchments. The N status of soils can impact on catchment loss of N (Stoddard and Traaen, 1995). The existence of large N pools within the soil means that microbial processes will not be N limited and, consequently, may contribute to N leaching (Johnson, 1992) and % soil N has been correlated with N leaching in empirical studies (Dise and Wright, 1995). Soil C:N ratios are also important with low ratios favouring nitrification and N breakthrough in forested catchments (Dise and Wright, 1995). These data were not available from soil survey datasets. With regard to land use, data relating to stand age (for forestry) and vegetation type would be useful. More generally, the use of catchment specific data (e.g. soil samples) would be preferable to the averaged, profile weighted data used to characterise the catchment soils. It would also be useful to examine sites where more frequent sampling has been undertaken so that the response data can approximate mean conditions and seasonal variation could be more accurately represented. The use of spot samples in this respect may lead to the modelling of unrepresentative responses. High density deposition monitoring data would also be useful to allow for variation in deposition data.

Conclusions

There is clear evidence of elevated NO_3^- concentrations due to N deposition within the study area. Similar levels in upland catchments have also been observed at regional and national scales (Allott *et al.*, 1995; Reynolds *et al.*, 1994). A significant contribution by NO_3^- to surface water acidity is apparent. Currently, this impact is greater outside the growing season, reflecting the seasonal dynamics of N cycling. Elevated N deposition levels may lead, initially, to increased NO_3^- concentrations outside the growing season when N uptake is lower and precipitation levels (and snowmelt) are more important (Mulder *et al.*, 1997). However, several sites in the study area are also impacted during the summer and if N loadings to these continue it may be that summer breakthrough will become more pronounced should deposition (and catchment N generation) exceed biological demand. Currently the catchments where N breakthrough appears to have occurred tend to be those at high altitude with limited soil and vegetation and thus low biotic retention capacity. These may already be in steady state with respect to N deposition and leaching.

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